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TITLE: PULSED PHOTOTHERMAL SPECTROSCOPY APPLIED TO LANTHANIDE AND ACTINIDE SPECIATION

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Pulsed photothermal spectroscopy applied to lanthanide and actinide speciation

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ABSTRACT

Several key elements important for the application of laser-based photothermal spectroscopies to the study of the complexation chemistry of lanthanides and actinides in solution have been demonstrated. The sensitivity of f-f electronic transition energies and band intensities to subtle changes in complexation was illustrated through comparison of visible and near infra-red absorption spectra of well-characterized U(IV) dimers with alkoxide ligands. Significant improvements in spectroscopic band resolution and energy measurement precision for solution species were shown to be achievable through work in frozen glasses at 77 K using a very simple cryogenic apparatus. A pulsed-laser photothermal spectroscopy apparatus was constructed and shown to be sensitive to optical density changes of 10^{-5} in an aqueous Nd^{3+} solution. In addition, the capability of obtaining photothermal lensing spectra of dilute actinide solutions in frozen glasses at 77 K was demonstrated.

1. INTRODUCTION

Developing an understanding of the complexation chemistry of toxic and radioactive metals under widely varying solution conditions is of central importance to determining the best strategies for assessing and cleaning up existing waste sites and for developing safe, long-term storage technologies. Laser-based techniques such as photothermal lensing (PTL) and photoacoustic (PAS) spectroscopies have the demonstrated sensitivity required to provide spectroscopic data at the low concentrations typical of environmentally relevant systems. This high sensitivity, in order to be fully exploited, must be combined with an empirical understanding of the spectroscopic manifestations of changes in complexation. In this paper we demonstrate the capabilities of our current instrumentation and describe our progress toward the realization of the potential of photothermal spectroscopy through work on well-characterized model complexes of U(IV).

The spectra of electronic transitions of the f elements in solution and in solid matrices contain information about the local environment of the metal center (ligation, solvation, etc.). The f-f absorption bands are reasonably narrow even in solution at room temperature, making small energy shifts with changes in complexation easily measurable. A number of workers have used lanthanides as probes of site variations by introducing them as substitutional impurities for metals which do not have such rich electronic structure.[1] Environmental concerns about the forms of actinide complexation under varying conditions in solution and in solid matrices lead us to a more direct interest in what their electronic structure can tell us.

The major barrier to the wide application of this approach is the complexity of the f element electronic structure and the consequent difficulty of understanding it in sufficient depth to evaluate the effects of the ligands. An understanding of the interactions which lead to the observed spectra even in well-characterized systems remains an actively pursued problem. The dimension of the problem remains beyond the reach of current electronic structure calculations.

A more empirical approach has promise of results in the near term. Unlike the transition metals that generally have partially filled d shells which can become involved in bonding, the lanthanides and actinides have their valence shells sufficiently shielded from the surrounding environment that variations in electronic structure with environment can be considered as perturbations on the dominant electronic structure of the free ion, rather than as the dominant factors controlling the f electron energy levels. If one can develop a large enough data set on the forms which these perturbations take for given types of ligands and coordination geometries, then one might be able to apply this knowledge to uncharacterized complexes.

Our approach is to conduct spectroscopic studies of well-characterized organometallic complexes of metal centers whose complexation resembles that expected for complexes of environmental interest. Understanding of the spectroscopic trends in these model complexes at some level will lead a to greatly increased utility for electronic structure studies of uncharacterized complexes. Comparison of the spectra obtained thus far demonstrates the potential of this approach.

For spectroscopic methods based on metal-center electronic structure to be useful in the study of real environmental problems, high sensitivity is required. The simple reason is that much relevant chemistry of concern for actinides takes place at concentrations in the nanomolar range, significantly below the sensitivity threshold of conventional, absorption-based spectroscopy. Photothermal techniques such as photoacoustic spectroscopy and photothermal lensing spectroscopy are laser-based methods which offer the requisite sensitivity in the wavelength range of interest. They have been adopted by a number of groups as the instrumental approaches most likely to give useful data at environmental concentrations. We briefly describe our implementation of photothermal lensing and its capabilities in the experimental section of this paper.

We have begun to apply photothermal techniques to both model complex studies and to relevant aqueous systems of higher complexity. In this paper we concentrate on the model complex studies, and discuss the aqueous systems only to the extent that they demonstrate the sensitivity of the spectroscopic methods. We also present and discuss a PTL spectrum at 77 K of a U(IV) complex in a frozen organic glass.

2. EXPERIMENTAL

2.1. Sample preparation

The two U(IV) complexes for which electronic spectra will be presented here are $KU_2(OtBu)_9$ and $U_2(OtBu)_8(HOtBu)$, where OtBu is tertiary butoxide ($OC(CH_3)_3$). The synthesis and structural characterization of these U(IV) complexes have been described elsewhere.[2,3] Data from x-ray crystallography and solution nmr spectra lead to the structures shown in Figure 1. Both dimers have two equivalent U centers with six-fold coordination by oxygen atoms in a roughly octahedral geometry. The potassium salt differs from the neutral species in that it has one less proton and the K^+ nearest to two of the bridging t-butoxide groups. The extra proton in the neutral dimer is known to be fluxional at room temperature and is believed to be localized primarily on the bridging t-butoxide groups.

The aqueous Nd^{3+} solution used to demonstrate the sensitivity of our PTL apparatus was prepared by diluting a 0.1 M $NdCl_3$ stock solution repeatedly with 0.1N HCl solution until a 10μM Nd^{3+} concentration was reached.

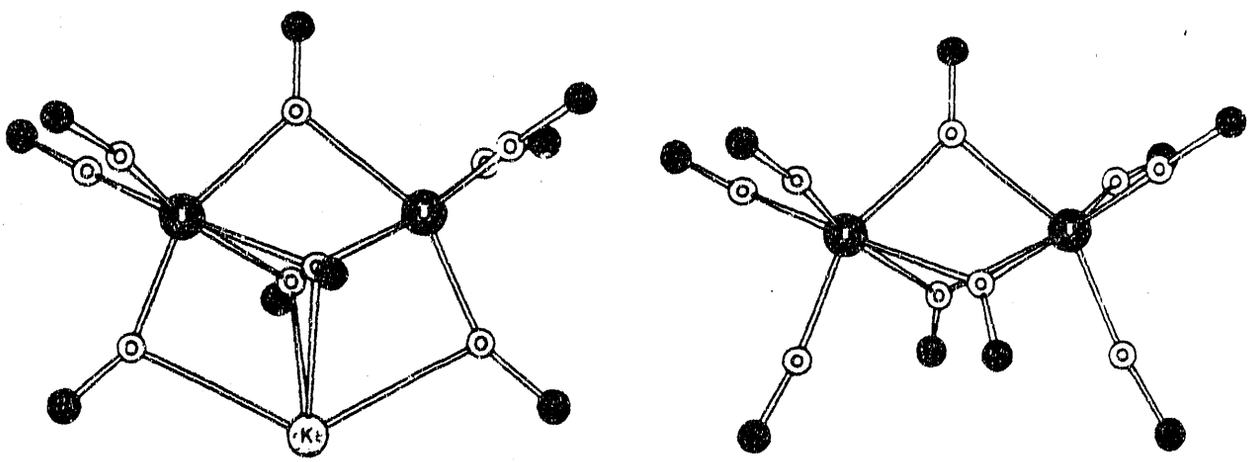

Figure 1: Backbone structures of the two U(IV) dimers used for spectroscopic work in this paper. The potassium salt is shown on the left and the protonated, neutral form is shown on the right. Only the oxygens and the tertiary carbon atoms are shown from the t-butoxide ligands. All are complexed to the U centers through the oxygens.

2.2. Absorption spectra

Absorption spectra of the U(IV) complexes in the visible and near infra-red regions were obtained with a Perkin Elmer Lambda 9 spectrometer. Working in a He atmosphere glove box, samples were dissolved in methylcyclohexane and placed in glass nmr or epr sample tubes (4mm or 2.5mm inner diameter) which were then sealed to prevent contamination by air. Low temperature spectra (77 K) were obtained by immersing the sample tubes in liquid nitrogen in a small dewar with a clear finger through which spectra could be taken. The methylcyclohexane froze into a clear glass at 77 K. The lensing effects of the cylindrical surfaces of the dewar and of the sample tube gave rise to non-zero baselines of the 77 K spectra, but this did not affect the measurements of the sample optical densities relative to the baseline.

2.3. Photothermal lensing

The principles and practical considerations involved in laser photothermal lensing spectroscopy have been described by others.[4] Our dual beam apparatus uses a pulsed dye laser pumped by a Nd:YAG laser (10 Hz, 10ns pulses) as the tunable source used to excite electronic transitions in the sample, while HeNe laser functions as the probe. A photodiode detector with low-noise amplification and high-pass frequency filtering is used to measure the intensity modulation of the HeNe beam following excitation of the sample by the pulsed dye laser.

Radiationless relaxation of the analyte following laser pumping of an electronic transition releases heat into the sample solution in the region through which the pump laser passes. The refractive index gradient resulting from the temperature-dependent index of refraction produces a negative lens in aqueous solution at room temperature. This transient lens defocuses the HeNe probe beam passing through it, and the defocusing is detected as a transient decrease in intensity of the center of the HeNe beam as detected in the far field by a photodiode behind a pinhole. The perturbation of the probe laser intensity at the detector is long-lived, having a typical lifetime of about 20 msec. A gated integrator is used to measure the intensity of the high-frequency front edge of the lens formation in time after the pump pulse.

We have used both a single cell configuration and the dual-cell, differential thermal lens technique as described by Erskine and Bobbitt.[5] The differential technique is useful in regions of high solvent absorbance, but we find that the experimental complexity which it introduces makes it less useful for routine work.

Low temperature PTL spectral acquisition was complicated by the presence of bubbling liquid N_2 in the optical path. High pass electronic filtering (3 kHz cutoff) of the PTL signal eliminated most of the noise associated with this phenomenon, but future plans include use of alternative cryostat designs which exclude liquid N_2 from the beam path.

3. RESULTS

3.1. Absorption spectra of U(IV) complexes

The visible and near IR absorption spectra in methylcyclohexane of the two U(IV) dimers shown in Fig. 1 are given in Figures 2 and 3. The spectra of these species are very similar, as one would expect if interactions with the ligands were relatively minor factors in determining the energy levels of the f orbitals. All of the major band features have a one-to-one peak correspondence between the two complexes and have similar relative energies. However, we also observe that even though the structural differences are quite subtle, the consequent shifts in band energies are easily measurable.

The 77 K spectra of the two U(IV) complexes in frozen methylcyclohexane glass are also shown in Figs. 2 and 3. Band widths are reduced by about a factor of three from the room temperature spectra, resulting in the resolution of a number of bands which had appeared only as shoulders in the room temperature spectra, and in the more precise determination of the energies of all of the bands.

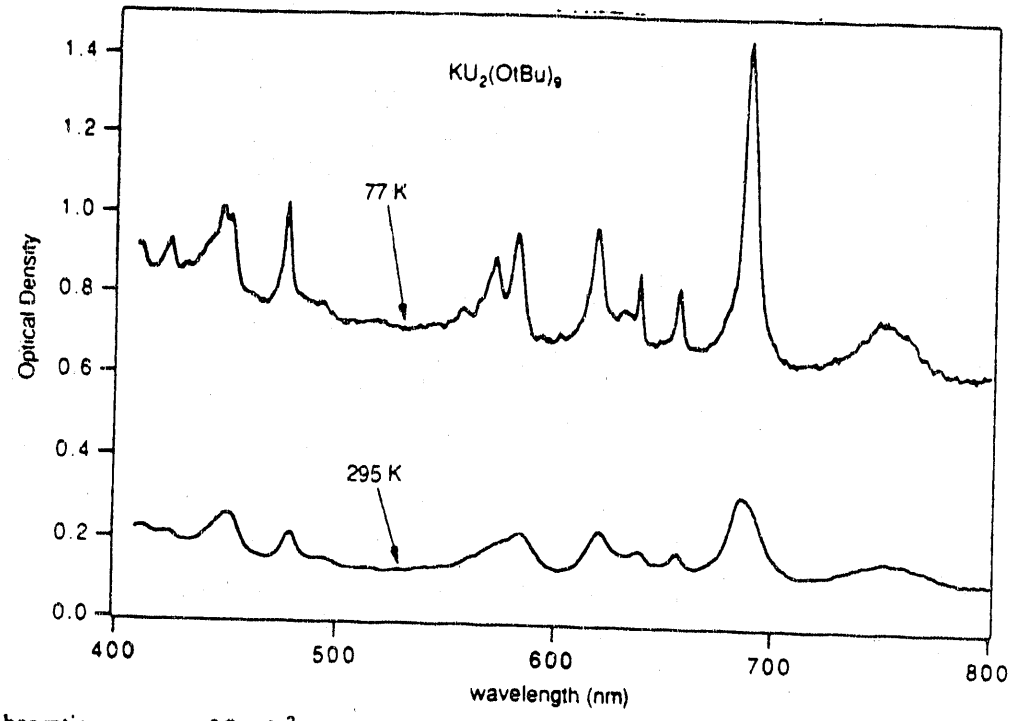

Figure 2: Absorption spectra of $8x10^{-3}$M $KU_2(OtBu)_9$ in methylcyclohexane at room temperature and at 77 K. Optical path lenght in sample cell is 2.5 mm.

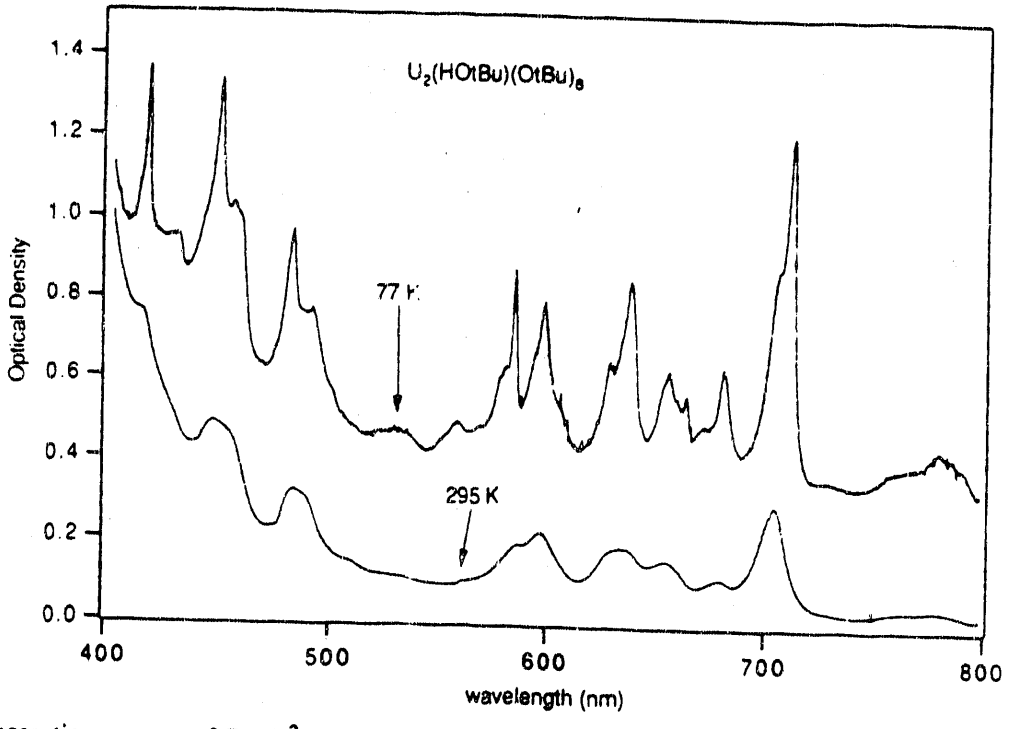

Figure 3: Absorption spectra of $7x10^{-3}$M $U_2(HOtBu)(OtBu)_8$ in methylcyclohexane at room temperature and at 77 K. Optical path length in sample cell is 4.0 mm.

3.2. Photothermal lensing spectra of dilute Nd^{3+}

The sensitivity of our PTL apparatus is demonstrated by the spectra of 10 μM Nd^{3+} solution shown in Figure 4. Three spectra are shown under the same excitation conditions. Fig. 4a shows a PTL spectrum of the Nd^{3+} solution using a single-cell arrangement. The peak at 520 nm is a Nd^{3+} transition with a molar absorptivity of 4 M^{-1} cm^{-1}. The slowly rising signal across the scan is due to water overtone absorption. This is illustrated by the spectrum of the solvent only in Fig. 4b. In Fig. 4c we show a spectrum taken with a dual-cell arrangement in which the water absorption is optically subtracted from the signal. These spectra demonstrate the capability to produce a S/N of 16/1 on the Nd^{3+} peak at 520 nm, which has a calculated absorptivity of 4 x 10^{-5} O.D. units at this concentration.

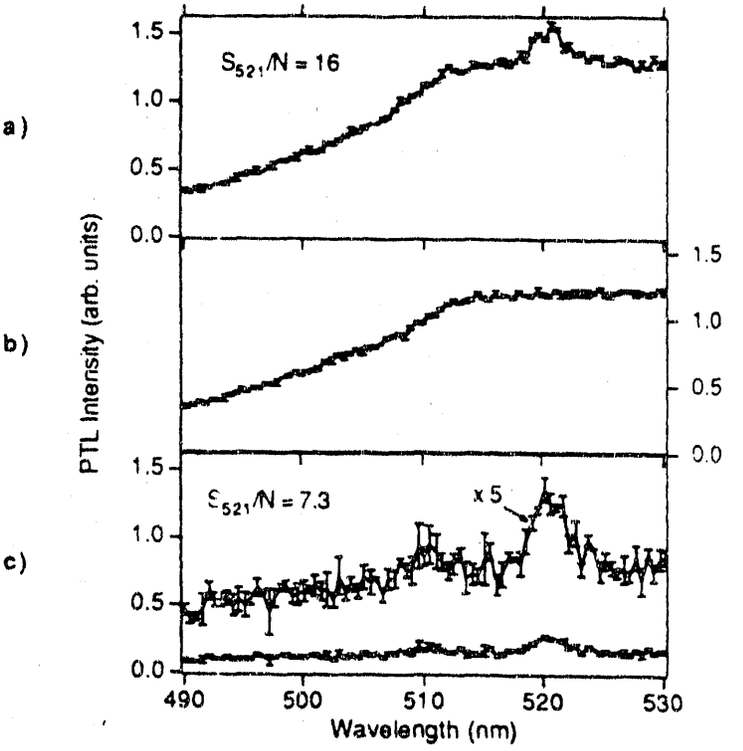

Figure 4: Photothermal lensing spectra of aqueous solutions: a) 10μM Nd^{3+} in 0.1N HCl; b) 0.1N HCl blank; c) 10μM Nd^{3+} in 0.1N HCl and 0.1N HCl blank in differential configuration.

3.3. Photothermal lensing spectra of U(IV) complexes

Figure 5 shows PTL spectra of a 5 x 10^{-3} M solution of $K_2U(OtBu)_9$ in methylcylcohexane at room temperature and at 77K. The spectral region scanned by the dye laser includes the strong absorption at 690 nm (see Fig. 2). By the standards of PTL the sample used to obtain the spectra in Fig. 5 was quite concentrated. The pulsed dye laser which was scanned to obtained these spectra was attenuated by 10^4 down to pulse energies below 1 μJ in order to avoid saturation.

We believe that these spectra demonstrate for the first time the capability of obtaining PTL spectra in frozen glasses.[6] We are proceeding with a more quantitative comparison of the temperature dependence of signal intensities in order to be able to obtain useful transition intensity information from PTL data. It is clear, however, that the improved resolution and precision in transition energy measurement available in the 77 K absorption spectra is immediately available in the low temperature PTL spectra as well.

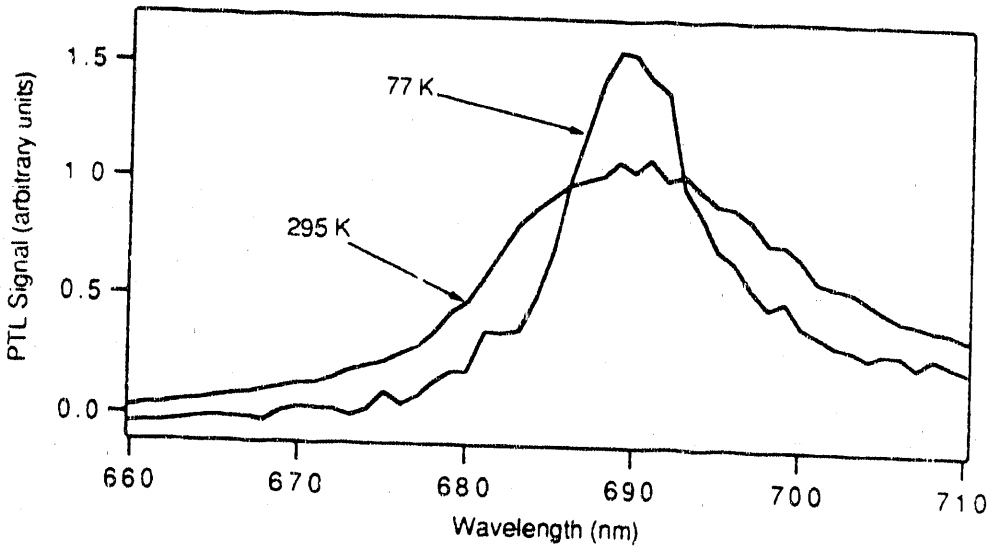

Figure 5: Photothermal lensing spectra of 5×10^{-3} M $KU_2(OtBu)_9$ in methylcyclohexane at room temperature and at 77 K. The relative vertical scaling is arbitrary due to differing alignment conditions for the two spectra.

4. DISCUSSION

In this paper we have demonstrated the sensitivity of f-f transitions to subtle changes in complexation of the metal center, substantial line narrowing and increased resolution of absorption lines in organic solvents upon cooling to 77K, PTL sensitivity with good signal to noise at 10^{-5} o. d. units, and the capability of obtaining PTL spectra of f-f transitions of actinides in frozen glasses.

Much work has been done in the past to demonstrate and improve the sensitivities of photothermal spectroscopies (PTL, PAS) to the point where they are capable of producing spectra of electronic transitions of actinides in solution at nanomolar concentrations. Less progress has been made on the equally important frontier of developing the capability to interpret the data thus obtained. We believe that a number of aspects of the current work contribute significantly to that effort.

Interpretation of the differences observed between the spectra of two U(IV) dimers will be the subject of a future paper which will include spectra of a broader range of complexes. Here we wish to make the simple points that there is a good one-to-one mapping of the bands between the two complexes and that there are measurable, and perhaps predictable, energy and intensity shifts with small changes in complexation. These observations support the expectation of a useful empirical interpretation of the spectra at some level.

The narrowing of the absorption bands with cooling to 77 K will allow the manifestation of even more subtle changes in complexation to be observed in the electronic spectra. These more precise energy measurements will also be invaluable in modeling the spectra. We are hopeful that we will be able to resolve vibronic structure upon further cooling to ~10 K.

Our demonstration that low temperature PTL spectra are easily obtainable and faithfully reproduce low temperature absorption results means that the advantages in interpretation of electronic structure afforded by low temperature spectra can be extended to work at low concentrations. It also has broader implications for extending the application of high-resolution and

non-linear laser spectroscopy to condensed phase systems for which laser-induced fluorescence is not a viable detection alternative.

5. ACKNOWLEDGEMENTS

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